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(54) Dispersing composition

(57) A composition comprises a mixture of alkali metal salts of a condensation product of naphthalenesulphonic acid and formaldehyde. The composition is useful for pigment dispersions, emulsion polymerisation, leather tanning, water treatment and cement fluidisation. The composition remains stable when stored in liquid form at low temperatures.

GB 2 106 527 A

SPECIFICATION
Dispersing composition

This invention relates to a novel dispersing agent composition. This invention also relates to a method for improving the properties of hydraulic cement-based mixtures by adding certain alkali metal salts of a condensation product of naphthalenesulphonic acid and formaldehyde to the cement mixture, such as cement paste, mortar, concrete, and the like.

Salts of condensation products of naphthalene-sulphonic acid and formaldehyde are effective for the dispersion of cement particles and such cement dispersing agents are commercially available.

The condensation product itself is generally prepared by sulphonating naphthalene with excess sulphuric acid and thereafter condensing the resulting naphthalenesulphonic acid with formaldehyde. The condensation product is then neutralised with an alkali metal hydroxide, e.g. sodium hydroxide, and the product is then treated to remove or reduce the water content. The commercial products, if not further processed, contain from about 5% to 22% by weight of sodium sulphate, on a dry basis. Sodium sulphate is present because the excess sulphuric acid employed in the sulphonation step is neutralised with sodium hydroxide. The sodium salt of the condensation products of naphthalene sulphonic acid and formaldehyde which are used as dispersing agents are frequently shipped, stored and added as liquid solutions. Sodium sulphate, the byproduct of the manufacture of the sodium salts of naphthalenesulphonic acid and formaldehyde condensation products, can precipitate as the decahydrate in cold weather, e.g. below about 18°C, depending on the concentration. The result is that the sodium sulphate decahydrate crystals clog tanks, dispensers, etc. and it is then impossible to properly handle the product.

The sodium sulphate salt can be eliminated by chilling and filtering or by neutralising with calcium hydroxide and filtering.

Richter, United States Patent 3,067,243, discloses a method of preparing salt free salts of naphthalenesulphonic acid-formaldehyde condensates.

Richter accomplishes the elimination of sodium sulphate by using an excess of naphthalene in the sulphonation step. This process, however, requires close monitoring throughout the reaction steps.

Johnson, United States Patent 3,277,162, discloses water-soluble salts of the condensation products of naphthalenesulphonic acid and formaldehyde. The cation of these salts may be sodium, potassium, calcium, or ammonium ions. Johnson, however, does not address the problem of precipitation of sodium sulphate decahydrate at low temperatures.

A dispersing composition according to the invention comprises a plurality of alkali metal salts of a condensation product of naphthalenesulphonic acid and formaldehyde. We find that, as a result of having a plurality of alkali metal salts, it is possible to overcome many of the problems of prior art compositions and in particular the composition can be capable of being stored in the form of a liquid at low temperatures even though it may contain a significant amount of sulphates, and in particular generally contains sodium sulphate. Whereas at low temperatures crystals of sodium sulphate decahydrate would normally gather at the bottom of the storage tank and clog dispensers and other equipment in the invention it is possible to avoid the formation of precipitates or solids that will adversely affect equipment. When the composition is used as a dispersing agent for concrete the properties of the concrete may equal or exceed those of concrete prepared with conventional dispersing agents.

The alkali metal salts generally present in the compositions of the invention are salts of sodium and potassium.

The condensation product of naphthalenesulphonic acid and formaldehyde which may be used in this invention can be prepared in such a manner as described below:

Naphthalenesulphonic acid is a well-known article of commerce. There are numerous methods of preparing naphthalenesulphonic acid. One method involves stirring one mole of naphthalene with 1 to 1.5 moles of concentrated sulphuric acid, for example 96% H_2SO_4, while heating to between 70°C to 175°C. It is well known that the temperature of the reaction influences the ratio of 1- and 2-naphthalenesulphonic acids in the end product. At temperatures between 70°C and 90°C., the naphthalenesulphonic acid comprises about 90% of 1-isomer and 10% of 2-isomer. At 110°C, about 75% of the 1-isomer is present and 25% of the 2-isomer; and at 140°C., the product is about 25% of 1-naphthalenesulphonic acid and 75% of 2-naphthalenesulphonic acid. The ratio of the two isomers in the naphthalenesulphonic acid is in no way critical to this invention. Either isomer or mixtures thereof can be used in this invention.

Formaldehyde, the other starting material used in this invention, is of course a well known chemical compound, and it is generally available as a water solution, usually in a concentration of 30% to 40% by weight. Such water solutions are preferred to produce the products of this invention. However, other sources of formaldehyde are also within the scope of this invention. These include paraformaldehyde and trioxane. Paraformaldehyde is a mixture of glycols having the formula $HO(CH_2O)_nH$ where n varies from about 8 to 100. It dissolves in water with depolymerisation and hydration to yield a solution of formaldehyde. Trioxane in aqueous solution in the presence of a strong acid such as the sulphuric acid used for sulphonating naphthalene is also depolymerised to provide

formaldehyde.

Naphthalenesulphonic acid and formaldehyde are condensed by heating at temperatures of about 60°C to 130°C. About 0.5 to 3 moles of formaldehyde are used for each mole of naphthalenesulphonic acid. The conventional method of preparing the condensation product calls for adding sodium hydroxide after the reaction has reached the desired degree of condensation. In the invention however a blend of salts is formed by adding both sodium hydroxide and, generally, potassium hydroxide. The sodium hydroxide may be added prior to the addition of the potassium hydroxide, or vice versa or they may be added simultaneously, for instance as a blend.

Alternatively, the sodium hydroxide and potassium hydroxide may be added to separate batches of condensation products of naphthalenesulphonic acid and formaldehyde, and the thus neutralised batches may be blended in the desired ratio.

The mole ratio of potassium hydroxide to sodium hydroxide may range from 1 to 3 moles potassium hydroxide to 1 mole sodium hydroxide with the result that the molar ratio potassium salts:sodium salts is from 3:1 to 1:1. The preferred mole ratio is about 2 moles potassium hydroxide to 1 mole sodium hydroxide.

The dispersing agent may be employed in either the form of dehydrated powder or in the form of an aqueous solution. In the area of cement dispersion, it may be added to the cement in an amount of about 0.1 to about 10 percent, based on the amount of cement.

The dispersing agent composition may be either pre-mixed as the dried from with the hydraulic cement or added to concrete, mortar, cement paste or the like at the time of mixing. It may be used alone or in combination with other auxillary agents such as a hardening accelerator, a retarder and an air entraining agent. It may also be used in pigment dispersions emulsion polymerisation, leather tanning, and water treatment and many other applications.

EXAMPLE 1

The condensation product of naphthalenesulphonic acid and formaldehyde was prepared according to method which is slightly modified from that disclosed in Tucker, United States Patent 2,141,569. The modified method is set forth below:

To 100 parts of concentrated sulphuric acid (specific gravity 1.84) contained in a suitable sulphonator and maintained at 160°C are added slowly with stirring 100 parts of refined naphthalene. After all of the naphthalene has been introduced (this operation generally requires about one hour), the mass is stirred at 160°C for four hours longer or until a test shows that substantially none of the naphthalene remains unsulphonated. The sulphonation mixture is then cooled to about 100°C and diluted with 44 parts of water to prevent solidification on subsequent cooling. The diluted material is further cooled at 80°C at which temperature 14.5 parts of a 40% aqueous solution of formaldehyde are added. This mixture is then stirred for three hours longer at 80°C.; but at the end of each successive hour there are added 14.5 parts more of formaldehyde solution, making a total at the end of the three hours of four portions of 58 parts in all. After all the formaldehyde has been added, the temperature is progressively raised over a period of one hour to 95—100°C. where it is maintained for 18 hours, while the mass is constantly stirred, or until a product of optimum effectiveness has been obtained. Experience has shown that when pure naphthalene is used, a final heating period of 18 hours yields the best product. Soon after the temperature has been raised to 95—100°C, it is found that substantially none of the aldehyde remains unconsumed in the condensation reaction. During the later stages of the 18 hour heating period, the mixture progressively thickens until at the end it generally reaches the consistency of thick molasses. If this thickening becomes so great, however, as to prevent proper stirring a small quantity of water may be added to keep the material liquid. After the desired degree of condensation has been reached, the mixture is then cooled.

Portions of the resulting condensation product were then neutralised with the following alkali metal hydroxides:

A) sodium hydroxide
B) sodium hydroxide: potassium hydroxide, 1:1 mole ratio
C) sodium hydroxide: potassium hydroxide, 1:2 mole ratio
D) sodium hydroxide: potassium hydroxide, 1:3 mole ratio

The alkali metal hydroxides were added at least until the naphthalenesulphonic acid-formaldehyde product was neutralised.

Each of the samples (A), (B), (C) and (D) was frozeon to —16°C and then was thawed gradually to 0.5 to 1°C.

The following Table sets forth properties of the slats produced by the addition of the above-mentioned alkali metal hydroxides:

TABLE 1

Sample	Mole Ratio Sodium hydroxide: potassium hydroxide	Volume of Container Occupied by Precipitate (%)	Character Of Precipitate
A	all sodium hydroxide	16	large, hard, needlelike crystals
B	1:1	6	amorphous, fluid floc
C	1:2	6	amorphous, fluid floc
D	1:3	32	amorphous, slightly fluid floc

Although the amount of precipitate in Sample D was relatively high, the precipitate was amorphous and slightly fluid. The dispersing agent formed with this sodium hydroxide:potassium hydroxide mole ratio is suitable for conventional storage and dispensing equipment.

EXAMPLE II

Six concrete mixtures, each of which contained 7690 g cement, 21,400 g 1.9 cm coarse aggregate, 17,650 g sand, and water as indicated in Table 2 were prepared. To these mixtures were added an air entraining agent (DARAVAIR, manufactured by W.R Grace & Co., Cambridge, Mass.) and the amounts and types of condensation product of naphthalenesulphonic acid and formaldehyde are indicated in Table 2.

Slump tests and compressive strength tests were conducted for each of the concrete samples. Percent air and weight per unit volume were also recorded for each sample of concrete. The results of the tests are set forth in Table 3.

TABLE 2

Sample	Brand Of Type I Cement	Water/ Cement Ratio	Air Entraining Agent (Fl. Oz. per 100lbs Cement)	Dispersing Agent	
				A	B
E	Universal Atlas, Hannibal	0.56	0.6	0.0	0.0
F	Universal Atlas, Hannibal	0.49	0.6	0.4	0.0
G	Universal Atlas, Hannibal	0.49	0.6	0.0	0.4
H	Ideal, Castle Hayne	0.58	0.7	0.0	0.0
I	Ideal, Castle Hayne	0.52	0.7	0.4	0.0
J	Ideal, Castle Hayne	0.54	0.7	0.0	0.4

A — sodium salt of condensation product of naphthalenesulphonic acid and formaldehyde.
B — sodium/potassium salt of condensation products of naphthalenesulphonic acid and formaldehyde [sodium/potassium mole ratio = 1:2].

TABLE 3

Sample	Slump (cm)	Air (%)	Unit Weight (pcf)	Compressive Strength (psi) 1 day	7day	28day
E	5.7	5.6	141.9	1194	2844	3990
F	5.1	5.0	143.8	2280	4058	4779
G	3.8	5.0	143.5	2248	4073	4891
H	7.6	5.2	142.4	1000	3248	3905
I	5.1	4.5	145.1	1291	4260	4980
J	5.7	4.5	145.1	1272	4053	4816

As clearly indicated in Table 3, the compositions employing the dispersing agent of the present invention, i.e. Samples G and J, exhibit properties which are essentially equal to the properties of samples which contain a conventional dispersing agent, Samples F and I, and exceed those of untreated concretes, Samples E and H.

CLAIMS

1. A dispersing composition comprising a plurality of alkali metal salts of a condensation product of naphthalenesulphonic acid and formaldehyde.

2. A composition according to claim 1 wherein the alkali metal salts are sodium salts and potassium salts.

3. A composition according to claim 2 wherein the molar ratio of sodium salts to potassium salts is from 1:3 to 1:1.

4. A composition according to claim 3 wherein the molar ratio of sodium salts to potassium salts is about 1:2.

5. A composition according to any preceding claim and that is in the form of an aqueous solution.

6. A composition according to claim 1 that includes sodium sulphate.

7. A method for preparing a dispersing composition according to claim 1 and which comprises the steps of:

(1) reacting sulphuric acid with naphthalene to obtain naphthalenesulphonic acid,
(2) condensing the naphthalenesulphonic acid with formaldehyde,
(3) neutralising the resulting condensation product of naphthalenesulphonic acid and formaldehyde with a neutralising agent comprising sodium hydroxide and potassium hydroxide.

8. A method according to claim 7 wherein the sodium hydroxide is added prior to the addition of the potassium hydroxide.

9. A method according to claim 7 wherein the potassium hydroxide is added prior to the addition of the sodium hydroxide.

10. A method according to claim 7 wherein the sodium hydroxide and potassium hydroxide are added simultaneously.

11. A method according to claim 7 wherein the sodium hydroxide is added to a first portion of the condensation product, the potassium hydroxide is added to a second portion of the condensation product, and the first and second portions of the condensation product are combined.

12. A method according to any of claims 7 to 11 wherein the molar ratio of sodium hydroxide to potassium hydroxide is about 1:3 to about 1:1.

13. A method according to claim 12 wherein the molar ratio of sodium hydroxide to potassium hydroxide is about 1:2.

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